Preprint
UCRL-JC-136270

Effect of Exhaust Temperature on NO_x Reduction by Nitrogen Atom Injection

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This article was submitted to
1999 Diesel Engine Emissions Reduction Workshop
Castine, Maine
July 5-8, 1999

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

October 28, 1999

EFFECT OF EXHAUST TEMPERATURE ON NO_x REDUCTION BY NITROGEN ATOM INJECTION

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Abstract

Chemical reduction of NO_x can be accomplished by injection of nitrogen atoms into the diesel engine exhaust stream. The nitrogen atoms can be generated from a separate stream of pure N_2 by means of plasma jets or non-thermal plasma reactors. This paper examines the effect of exhaust temperature on the NO_x reduction efficiency that can be achieved by nitrogen atom injection. It is shown that to achieve a high NO_x reduction efficiency at a reasonable power consumption penalty, the exhaust temperature needs to be 100°C or less.

Introduction

Nitrogen atoms, N, can be used for the chemical reduction of NO to N_2:

$$N + NO \rightarrow N_2 + O \qquad (1)$$

Dissociating the N_2 component of the exhaust stream can generate the N atoms. The N_2 molecules can be dissociated thermally using a plasma jet [ref. 1-2]. Electron-impact reactions in a non-thermal plasma reactor can also be used to dissociate the N_2 molecules [ref. 3-8].

The first problem in utilizing reaction (1) is the expense of producing the N atoms. The dissociation energy of N_2 is very large, and a large amount of power is required to produce a supply of N atoms sufficient to reduce even very dilute concentrations of NO from the exhaust stream [ref. 1, 8]. This problem may not be so severe for modern light-duty diesel engines with NO_x emissions of 100 ppm or less. Under non-thermal plasma conditions ideal for maximum N_2 dissociation, Penetrante *et al.* [ref. 3] measured a reduction of 6.25 ppm of NO per Joule/liter (J/L) of input electrical energy density. Assuming that each 10 J/L corresponds to around 1% of the engine power output, the measurements in ref. [3] suggests that it is possible to reduce 100 ppm of NO using only 1.6% of the engine power output.

The second problem in utilizing reaction (1) arises because of the dissociation of O_2 in the exhaust stream. The dissociation energy of O_2 is smaller than that of N_2. It is therefore highly probable that the energy in the plasma will be spent mostly in the production of O atoms rather than N atoms. The O atoms will simply oxidize NO to NO_2,

$$O + NO + M \rightarrow NO_2 + M \qquad (2)$$

and the total NO_x reduction will be small. To avoid this problem, the generation of N atoms from a separate stream of pure N_2 has been suggested [ref. 1-2, 9]. In this case the plasma produces only N atoms, which are then injected into the NO_x- and O_2-containing exhaust stream.

The third problem in utilizing reaction (1) arises from reactions of the injected N atoms with the O_2 in the exhaust stream. The N atoms injected into the exhaust stream can react with O_2 to produce NO:

$$N + O_2 \rightarrow NO + O \tag{3}$$

With a plasma jet, reaction (3) is fast at the temperature at which N_2 dissociation becomes appreciable. It is imperative that the N atoms are formed at high temperatures but used only at low temperatures. Ref. [1] discusses a plasma jet technique in which only a small fraction of the N_2 is heated to very high temperatures by direct contact with the plasma arc and the hot gas pockets are interspersed with layers of cold N_2 into which N can diffuse. In a non-thermal plasma, the electron-impact dissociation of N_2 can be accomplished at low temperatures [ref. 3, 7].

Even with a relatively cold source of N atoms, reaction (3) can become a problem at typical diesel engine exhaust temperatures. This paper examines the effect of reaction (3) on the NO_x reduction efficiency at various exhaust temperatures. The objective is to determine the exhaust temperature necessary for efficient implementation of N atom injection for NO_x reduction.

Results

Electron-impact dissociation of N_2 in a non-thermal plasma is the best way of producing N atoms at low gas temperatures. The electrical energy requirements for N atom production in various types of non-thermal plasmas have been measured by Penetrante *et al.* [ref. 3]. The important control parameter that determines the number of N atoms produced in the plasma is the electrical energy density (in units of J/L), which is defined as the power (W) delivered to the plasma divided by the gas flow rate (L/s). The best non-thermal plasma reactor produces 6.25 ppm of N atoms per J/L of energy density delivered to the plasma. If all the N atoms are utilized in the reduction of NO according to reaction (1), then it is possible to reduce 100 ppm of NO with a plasma energy density of 16 J/L.

Figure 1 shows the chemical kinetics calculation of the concentrations of NO and NO_2 during N atom injection into a gas mixture containing 100 ppm NO, 10% O_2, balance N_2, at a gas temperature of 50°C. It has been assumed that the plasma produces 6.25 ppm of N atoms per J/L of energy density. Most of the N atoms are consumed in reaction (1). At a gas temperature of 50°C, only a very small fraction of the N atoms are consumed in the production of NO according to reaction (3). About 90% NO_x reduction can be achieved with 20 J/L of plasma energy density. A small amount of NO is oxidized to NO_2 according to reaction (2) as a result of the O atom that is produced by reaction (1). As the energy density is increased, any NO_2 is eventually reduced back to NO by the O atoms:

$$O + NO_2 \rightarrow NO + O_2 \tag{4}$$

All the NO_x is eventually reduced when a sufficient amount of N atoms is injected at the low gas temperature. It is possible to obtain 100% NO_x reduction provided the gas temperature is kept low.

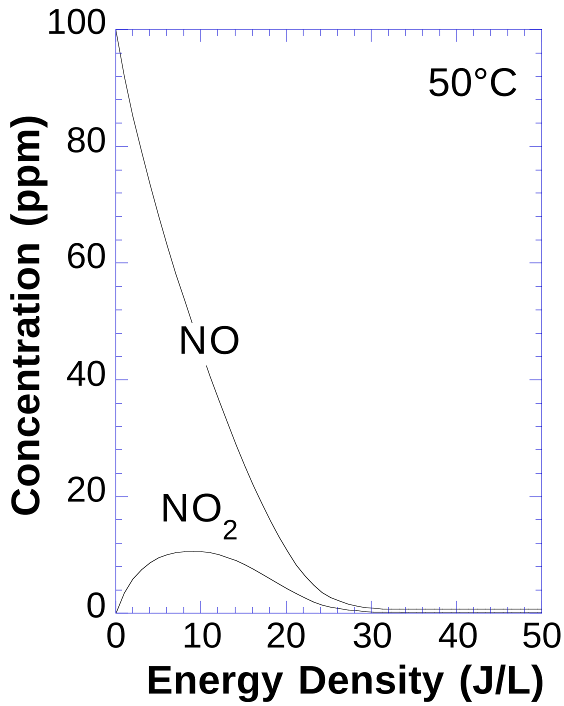

Figure 1. Chemical kinetics calculation of the concentrations of NO and NO_2 during nitrogen atom injection into a gas mixture containing 100 ppm NO, 10% O_2, balance N_2, at a gas temperature of 50°C.

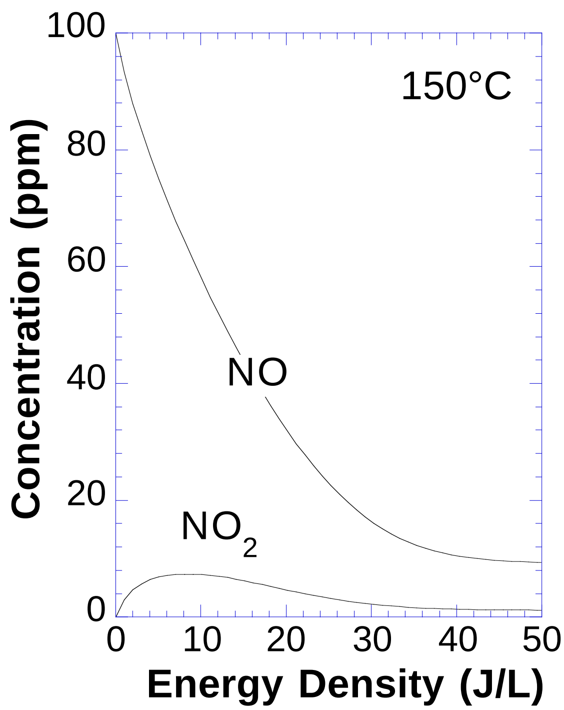

Figure 2. Chemical kinetics calculation of the concentrations of NO and NO_2 during nitrogen atom injection into a gas mixture containing 100 ppm NO, 10% O_2, balance N_2, at a gas temperature of 150°C.

Figure 2 shows the chemical kinetics calculation of the concentrations of NO and NO_2 during N atom injection into a gas mixture containing 100 ppm NO, 10% O_2, balance N_2, at a gas temperature of 150°C. A greater amount of the N atoms is consumed in the production of NO according to reaction (3). It is no longer possible to obtain greater than 90% reduction at this gas temperature.

Figure 3 shows the chemical kinetics calculation of the concentrations of NO and NO_2 during N atom injection into a gas mixture containing 100 ppm NO, 10% O_2, balance N_2, at a gas temperature of 250°C. A large number of the N atoms is consumed in the production of NO. The maximum NO_x reduction efficiency that can be achieved at this gas temperature is only 50%. With energy densities less than 50 J/L, the NO_x reduction efficiency that can be achieved is less than 50%.

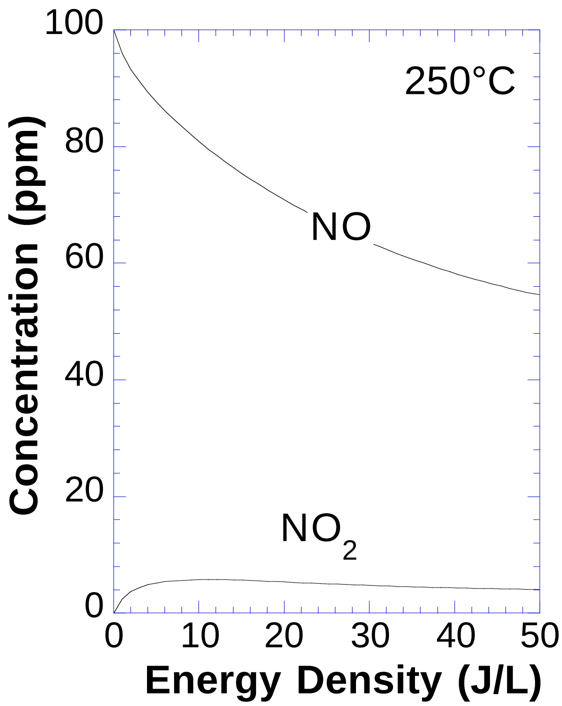

Figure 3. Chemical kinetics calculation of the concentrations of NO and NO_2 during nitrogen atom injection into a gas mixture containing 100 ppm NO, 10% O_2, balance N_2, at a gas temperature of 250°C.

Conclusions

N atom injection can be useful for chemically reducing NO_x in diesel engine exhaust. Because of the large amount of power required to produce a sufficient supply of N atoms, this technique is most applicable to modern light-duty diesel engines for which the NO_x emissions is already 100 ppm or less. To achieve a high NO_x reduction efficiency at a reasonable power consumption penalty, the exhaust temperature needs to be 100°C or less.

Acknowledgments

This work was performed at Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under Contract Number W-7405-ENG-48, with support from the Chemical Sciences Division of the DOE Office of Basic Energy Sciences.

References

[1] Behbahani, H.F., Fontijn, A., Muller-Dethlefs, K. and Weinberg, F.J., “The Destruction of Nitric Oxide by Nitrogen Atoms from Plasma Jets”, *Comb. Sci. Technol.* **27**, 123 (1982).

[2] Behbahani, H.F., Warris, A.M. and Weinberg, F.J., “The Destruction of Nitric Oxide by Nitrogen Atoms from Plasma Jets: Designing for Thermal Stratification”, *Comb. Sci. Technol.* **30**, 289 (1983).

[3] Penetrante, B.M., Hsiao, M.C., Merritt, B.T., Vogtlin, G.E., Wallman, P.H., Kuthi A., Burkhart, C.P., and Bayless, J.R., “Electron-Impact Dissociation of Molecular Nitrogen in Atmospheric-Pressure Non-Thermal Plasma Reactors”, *Appl. Phys. Lett.* **67**, 3096 (1995).

[4] Penetrante, B.M., Hsiao, M.C., Merritt, B.T., Vogtlin, G.E. and Wallman, P.H., “Comparison of Electrical Discharge Techniques for Non-Thermal Plasma Processing of NO in N_2”, *IEEE Trans. Plasma Sci.* **23**, 679 (1995).

[5] Penetrante, B.M., Hsiao, M.C., Merritt, B.T., Vogtlin, G.E., Wallman, P.H., Neiger, M., Wolf, O., Hammer, T. and Broer, S., “Pulsed Corona and Dielectric-Barrier Discharge Processing of NO in N_2”, *Appl. Phys. Lett.* **68**, 3719 (1996).

[6] Hsiao, M.C., Penetrante, B.M., Merritt, B.T., Vogtlin, G.E. and Wallman, P.H., “Reduction of NO_2 in N_2 by Non-Thermal Plasmas”, *J. Adv. Oxid. Technol.* **2**, 283 (1997).

[7] Penetrante, B.M., Hsiao, M.C., Merritt, B.T., Wallman, P.H. and Vogtlin, G.E., “NO_x Reduction by Compact Electron Beam Processing”, *Proceedings of the 1995 Diesel Engine Emissions Reduction Workshop*, La Jolla, CA (July 1995).

[8] Penetrante, B.M., Hsiao, M.C., Merritt, B.T. and Vogtlin, G.E., “Fundamental Limits on NO_x Reduction by Plasma”, *SAE Paper 971715* (1997).

[9] Bittenson, S.N. and Becker, F.E., “Direct Chemical Reduction of NO_x in Diesel Exhaust”, *SAE Paper 982515* (1998).